

Equation Chapter 1 Section 1 Clustering and segregation of small vacancy clusters near tungsten (0 0 1) surface

Guohua Duan^{1,2†}, Xiangyan Li^{1†}, Yichun Xu¹, Yange Zhang¹, Yan Jiang¹, Congyu Hao^{1,2}, C.S. Liu^{1*}, Q.F. Fang¹, Jun-Ling Chen³, G.-N. Luo³, Zhiguang Wang⁴

¹Key Laboratory of Materials Physics, Institute of Solid State Physics, Chinese Academy of Sciences, P.O. Box 1129, Hefei 230031, PR China

²University of Science and Technology of China, Hefei 230026, PR China

³Institute of Plasma Physics, Chinese Academy of Sciences, Hefei 230031, PR China

⁴Institute of Modern Physics, Chinese Academy of Sciences, Lanzhou 730000, PR China

[†]These authors contributed equally to this work.

E-mail address: csliu@issp.ac.cn (C.S. Liu)

Abstract

Nanoporous metals have been shown to exhibit radiation-tolerance due to the trapping of the defects by the surface. However, the behavior of vacancy clusters near the surface is not clear which involves the competition between the self-trapping and segregation of small vacancy clusters (V_n) nearby the surface. In this study, we investigated the energetic and kinetic properties of small vacancy clusters near tungsten (0 0 1) surface by combining molecular statics (MS) calculations and object Kinetic Monte Carlo (OKMC) simulations. Results show that vacancies could be clustered with the reduced formation energy and migration energy of the single vacancy around a cluster as the respective energetic and kinetic driving forces. The small cluster has a migration energy barrier comparable to that for the single vacancy; the migration energy barriers for V_{1-5} and V_7 are 1.80, 1.94, 2.17, 2.78, 3.12 and 3.11 eV, respectively. Clusters V_2 and V_3 become unstable near surface (0 0 1) and tend to dissociate into the surface. At the operation temperature of 1000 K, the single vacancy, V_2 , V_3 and V_4 were observed to segregate to the surface within a time of one hour. Meanwhile, larger clusters survived near the surface, which could serve as nucleating center for voids near the surface. Our results suggest that under a low radiation dose, surface (0 0 1) could act as a sink for small vacancy clusters, alleviating defect accumulation in the material under a low radiation dose. We also obtained several empirical expressions for the vacancy cluster formation energy, binding energy, and influence radius as a function of the number of vacancies in the cluster.

Keywords: Vacancy cluster; Nanoporous tungsten; Radiation-resistance; Segregation

1. Introduction

In future fusion nuclear reactors and advanced fission reactors, nuclear materials are exposed to a hostile environment involving intense heat fluxes, high temperatures and extreme fluxes of high-energy neutrons radiation [1]. Radiation exposure displaces atoms violently from their lattice sites, and produces point defects (interstitials and vacancies) and defect clusters, which may subsequently evolve into dislocation loops, voids and bubbles. Such microstructural change not only deteriorates the macroscopic properties of irradiated materials, but also severely degrades their performance and lifetime limits. In particular, voids, as a result of vacancy accumulation and growth, lead to swelling and eventual material failure [1–5]. Irradiation resistance is thus a major requirement for designing advanced nuclear materials in fusion reactors [6].

Concerning radiation tolerance, it is widely accepted that a variety of interfaces, e.g. surfaces in nanoporous (NP) materials and grain boundaries in nano-crystals can provide sinks for defects from radiation, and thus enhance the radiation tolerance [7–18]. For instance, irradiation experiments suggest that NP metals exhibit radiation-resistance [7–10]. By using in situ Kr-ion irradiation technique, Sun et al. observed frequent removal of various types of defect clusters by free surfaces in NP silver (Ag) [13]. They found, opposite to conventional wisdom, both types of diffusivities are lower in NP Ag due to the reduced interaction energy between isolated defect clusters in NP Ag. The void formation is expected to be suppressed as vacancies are absorbed by surfaces, since voids are developed through vacancy agglomeration [3]. However, the theoretical investigation of the vacancy cluster behavior in NP metals is limited (most of efforts have been made to investigate the vacancy or vacancy cluster behavior in the bulk material [19–25]). The evolution of the vacancy near the surface involves the competition of the clustering and segregation of vacancy clusters near the surface.

As illustrated in Fig. 1, on one hand, vacancies could diffuse towards the surface and get trapped there. On the other hand, vacancies could also be clustered on the way to the surface. Determination of kinetics of defect clusters near the surface is essential to understand and model their migration and clustering in irradiated materials. In this work, NP tungsten (W) was chosen as a model system considering its engineering application as plasma facing materials and divertor armor in fusion reactors [26–28]. We investigated the energetic and kinetic properties of vacancy cluster and its nearby mono-vacancies in W on the atomic scale by using molecular statics (MS) simulations, including formation energy, migration barrier, binding energy and influence radius. With the energetic and kinetic parameters as input, the diffusion of the vacancy cluster near W (0 0 1) surface at 1000 K at long timescale was then investigated by object Kinetic Monte Carlo method (OKMC) [29]. We show that, although vacancies could be clustered near the surface, small clusters still segregate to the surface due to high mobility comparable to that for the single vacancy.

2. Computational method

2.1. Interatomic potential and surface models for MS simulations

The bond-order potential (BOP) [30] was employed to describe atomic interaction among W atoms. The potential well describes the energetics and kinetics of point defects in W bulk. In bulk W, formation energy is 3.75 eV for the single vacancy and 10.19 eV for the self-interstitial atom of <1 1 1> crowdion. The migration barrier of the vacancy is 1.80 eV and 0.002 eV for the self-interstitial atom. The potential has been used for studying radiation effects in W [17].

The BOP includes three-body contributions and angular dependence and thus it is time-consuming to perform simulations by using this potential. To increase the computational efficiency, we built two types of models. A bulk W model containing 5,488 atoms was constructed with a size of $14 \times 14 \times 14$ (or $44.39 \times 44.39 \times 44.39 \text{ \AA}^3$), where a_0 is the lattice constant of 3.171 Å. Periodic boundary conditions were imposed in all directions. The model has been checked to be large enough to investigate the energetic and kinetic behavior of small vacancy clusters.

A (0 0 1) surface model containing 2,000 atoms was constructed with a size of $10a_0$ in each direction. Periodic boundary conditions were imposed in [1 0 0] and [0 1 0] direction. A vacuum layer with a thickness of 15 Å was added in the [0 0 1] direction. The relaxed surface model is presented in Fig. 1. The size in the direction normal to the surface is large enough to avoid the interaction of the vacancy cluster with the other surface on the opposite side of the surface.

2.2. Definition and calculations of defect properties

The formation energy of a vacancy cluster was defined as:

$$E_f = \frac{E_{\text{relaxed}} - E_{\text{bulk}}}{n}, \quad (1)$$

where E_{relaxed} and E_{bulk} are the total energies of the relaxed model with and without a vacancy cluster, respectively; E_{bulk} is the atomic cohesive energy (−8.89 eV) of a bulk lattice W; n is the number of vacancies in the cluster. The system was relaxed by employing the steepest descent method.

The binding energy of a vacancy with a vacancy cluster was defined as:

$$E_b = E_{\text{relaxed}} - E_{\text{bulk}} - E_f, \quad (2)$$

where E_{bulk} is the bulk vacancy formation energy (3.75 eV). A positive value of the binding energy indicates that it is energetically favorable for a mono-vacancy to locate near the cluster.

The migration of small vacancy clusters in the bulk and near the surface was investigated by the nudged elastic band (NEB) method [31], which determined the saddle point and the migration barrier. There are 30 image states on the initial migration path.

2.3. Details for OKMC simulations of vacancy evolution near the surface

The kinetics of vacancy clusters near the surface was simulated by a standard OKMC method [29]. This technique allows us to follow the evolution of all the vacancy-type defects considered here, to take into account their spatial correlation and to cover the appropriate time and length scales. The input data for the OKMC include the energetic and kinetic properties of the vacancy clusters and the interaction range, which were generated by MS calculations. In the OKMC model, defects were

considered as objects characterized by their space coordinates, nature (V and V_n in this study), shape (spherical here), mobility and dissociation rate. The diffusion processes for mobile defects were treated in a specific and efficient way: the details of the atomic transport were ignored and the jumps of the mobile species were bunched into single diffusion events.

We used cubic simulation cells with a side of 20 nm. The upper and lower surfaces of the cell are defect sinks. As we investigated the behavior of a single vacancy cluster, the cluster was put at the center of the cell. The system temperature was chosen as 1000 K, which is the typical operation temperature of W in a fusion reactor [27]. As we explored the clustering and segregation of the vacancies near the surface, multiple vacancies were randomly generated. The initial concentrations of single vacancies were given two values of 100 and 300 appm, respectively.

3. Results and discussion

3.1. MS investigation of the formation of small vacancy clusters in W bulk

We begin with finding the stable configuration for a vacancy cluster. Strictly speaking, for a given size of the cluster, it should reconsider the energy of all the different configurations to find the most stable one. However, such procedure can be very time consuming computationally due to multiple configurations of a vacancy cluster. The stable configuration for a vacancy cluster V_n was obtained by minimizing the system energy with a vacancy introduced at a particular site near the V_{n-1}. Moreover, we only searched the configurations for small vacancy clusters (V_n, n=1–7). The corresponding configurations for the vacancy clusters can be seen in Fig. 2(a). We found that most of the vacancy clusters configurations are consistent with that in Ref. [30]. Note that, previously [30], Ahlgren et al. proposed that if any of the eight nearest atoms are missing for a particular W atom, the calculated total potential energy increases. The minimum energy configuration for a vacancy cluster should thus be a configuration where the total number of nearest neighbors in the lattice is at its maximum. Total energy calculations are thus needed only for those cluster configurations that result in a small number of broken W bonds. Nevertheless, the lowest energy configuration for a cluster of five vacancies is different from the square pyramid shape in Ref. [30], but consistent with the recent density functional theory result [32]. The formation energy for the present configuration is 1.28 eV lower than that in Ref. [30]. Therefore, such criteria may only apply for certain vacancy clusters.

Fig. 2(b) shows the formation energies of vacancy clusters in the bulk as a function of the cluster size n . For a large void, is proportional to the surface energy of the void. Assuming the void to be spherical, it can be deduced that has the form. As suggested in the continuum models describing void formation and growth during crystal growth [33], here parameter A is an effective surface energy for a cluster containing n vacancies. For the present small vacancy clusters, they should deviate from the classical $n^{2/3}$ energy scaling behavior. Fitting the formation energies for vacancy clusters in bulk W

with the same power-law results in the following equation:

$$= 4.1562n^{0.7159}. \quad (3)$$

According to Eq. 2, the binding energy of a vacancy with a cluster is approximated by:

$$E_b^{V-V_n} = 4.1562[n^{0.7159} - (n+1)^{0.7159}] + 3.75. \quad (4)$$

To check the prediction ability of this equation, we compared the MS results of the binding energy obtained according to Eq. 2 with the predictions by Eq. 4, as shown in Fig. 3. Note that, for a small V_n ($n < 10$), the binding energy was derived from V_n formation energy (Eq. 2), while for a large V_n , e.g. V_{50} , the bind energy was obtained by calculating the vacancy formation energy around the cluster (the reduction in the formation energy was binding energy). It can be seen from Fig. 3, Eq. 4 well describes the vacancy binding energy with the V_n as a function of n , although Eq. 4 overestimates the binding energy of the V with V_2 .

In addition to the binding energy, we also calculated the influence range of the V_n . Within the influence region, the V formation energy derivates from a bulk by at least 0.1 eV. By fitting the range to n , we found the range R approximately depends on n linearly as. The influence range for V_2 and V_3 was overestimated by such formula, but the formula well describes the vacancy cluster size dependence of R for other cases.

3.2. MS investigation of the diffusion of small vacancy clusters in W bulk

With the stable configurations of the clusters in hand, next we investigated their migration mechanisms to obtain the corresponding energy barrier. The vacancy clusters were assumed to migrate by successive nearest-neighbor mono-vacancy jumps. This motion may require passing through metastable intermediate states (see for example, V_2 , V_4 , V_5 and V_7). The migration energies are size-dependent: 1.80, 1.94, 2.17, 2.78, 3.12 and 3.11 eV for $n = 1, 2, 3, 4$ and 7 respectively (Fig. 4). For V_6 (Fig. 2(a)), we found there are no one or two nearest-neighbor mono-vacancy jumps for V_6 to migrate from one stable configuration to another one due to a high-symmetric octahedral configuration. We emphasize that the low values are obtained for V_3 and V_4 comparable to that for the single vacancy. Larger V_n clusters are believed to be immobile.

To well understand the mobility of the small V_n at an elevated temperature, we calculated the transition time of V_n at 1000 K, which is a typical operation temperature for W in a fusion reactors [27]. As shown in Fig. 5, the time for small ($n < 5$) to jump one step is less than 10^2 s, implying such V_n has a not so low mobility. In other words, ($n < 5$) can play an important role in cluster aggregation and growth or can diffuse into the surface. The transition time for V_5 and V_7 is longer than 10^3 s. Thus, the two clusters basically remain immobile at 1000 K.

3.3. MS investigation of the formation and diffusion of mono-vacancies around the vacancy cluster

To understand the clustering of the vacancy, we explored the interaction between a vacancy

cluster and nearby mono-vacancies in terms of the influence of the vacancy cluster on the formation energy and migration energy barrier of nearby mono-vacancies. Fig. 6 presents the formation energies of mono-vacancies in the vicinity of the V_n as a function of the distance of the vacancy from the cluster center. It can be seen, as a vacancy approaches to the cluster, its formation energy basically reduces. Thus, it is energetically favorable for a mono-vacancy to locate near a vacancy cluster and bind with the cluster into a new larger cluster. Meanwhile, the maximum reduction in the formation energy of mono-vacancies is cluster size dependent.

The kinetics for mono-vacancies migration around vacancy clusters was further calculated by using the NEB method [31]. As shown in Fig. 7, the diffusion energy barrier for the single vacancy around near a V_n depends on the migration path. There are always exist low energy barrier migration path for the vacancy to approach the V_n . For example, the mono-vacancy has a barrier as low as 0.22 eV on one path near V_3 . Such low energy barrier indicates the mono-vacancy far away from the cluster prefers to migrate towards the cluster kinetically. We also found that the energy barrier on some migration paths is higher than that for the single V diffusion in a perfect bulk W. Nevertheless, the average diffusion energy barrier for the V nearby the V_n is reduced (Fig. 7(g)). Furthermore, it shows a decreasing trend with n , indicating that a larger V_n accelerates diffusion of the V more greatly. Meanwhile, the barrier for the V is lower than that for the V_n . Thus, a V_n could be considered as a static sink for the V near itself.

3.4. MS investigation of the diffusion of small vacancy clusters near W (0 0 1) surface

A small V_n ($n=1-3$) has a high mobility comparable to that for the single vacancy (Fig. 4). Next, we explore the diffusion and segregation of V_2 and V_3 near a W (0 0 1) surface by calculating the formation energy and diffusion energy barrier of V_2 and V_3 . Fig. 8 represents the results for V_2 . Initially, was placed at different sites near the surface as shown in Fig. 8(a). V_2 contains two vacancies that are first-nearest neighbors. We designed several paths for V_2 migration towards the surface. As V_2 is far away from the surface, its formation energy remains a constant bulk value. Only when V_2 is within a range of about 6.0 Å, V_2 formation energy varies. Along the path AB-BC-CD-DE-EF-FG-GH-HI, V_2 first remains its bulk configuration and then becomes another configuration on the surface. The energy profile on this path is firstly increasing and then decreasing. The V_2 formation energy with a configuration of FG is about 1.5 eV higher than that for a bulk V_2 . Along the path AB-BC-CD-DE-EF1-EH1-F1H1-G1H1-H1I1, V_2 dissociates from a bulk configuration and then locates on the surface; vacancy clusters were also observed to dissociate near an iron grain boundary [34]. The energy profile along the path is basically decreasing. Therefore, it is therefore energetically favorable for V_2 to locate at the surface. During the segregation process, V_2 undergoes configurational transition. Furthermore, V_2 on the surface contains two vacancies that are second-nearest neighbors, while in the bulk the two vacancies in V_2 are first-nearest neighbors. After a bulk V_2 segregates to the atomic layers near the surface, the system energy decreases by about 3 eV. As V_2 transits from a

configuration of GH (or G1H1) near the surface to a configuration of HI (or H1G1) on the surface, the system energy further reduces by about 3 eV.

To show whether it is kinetically favorable for V_2 to segregate to the surface, we also calculated the migration energy landscape of V_2 near the surface. As shown in Fig. 8(c), V_2 has a migration energy barrier of 1.94 eV as located in the bulk region (Fig. 4). But the energy landscape near the surface is rough. Except for the energy barrier from DF to EF/EF1, the barriers along other paths are smaller compared with the bulk diffusion energy barrier of V_2 . For example, V_2 of F1H1 overcomes an energy barrier of 1.38 eV to locate at G1H1, which then nearly barrier-freely segregates to the surface along path G1H1-H1I1. It is thus kinetically favorable for V_2 to migrate towards the surface and reside therein. Previously [35], for the single vacancy, we have shown that the appearance of a high energy barrier near the surface causes the vacancy to try many times to segregate to the surface. We expect that a V_2 at AB will behave similarly, while a V_2 at EF will take a directed walk towards the surface.

Fig. 9 presents the energetic and kinetic properties of V_3 near the (0 0 1) surface. The initial configuration of V_3 is ABC, taken from Fig. 2. The computational procedure is similar to that for V_2 . We found both the formation energy profile and diffusion energy barrier landscape near the surface are similar to that for V_2 . After V_3 segregates from ABC to HH1I on the surface along a diffusion-dissociation-segregation path, the system energy reduces by about 8.5 eV. Therefore, there is also an energetic driving force for V_3 to migrate to the surface from the bulk. Near the surface, the energy barrier is significantly lower than that for V_3 diffusion in the bulk. It is thus energetically and kinetically favorable for V_3 to enter the surface from the bulk.

3.5. OKMC investigation of clustering and segregation of the vacancy near W (0 0 1) surface

The above MS calculations provide atomic insight into the vacancy cluster behavior near the surface. To well understand the clustering and segregation of the vacancy near the surface at long timescale, we performed OKMC simulations at 1000 K. We found that, a single V_1 , V_2 , V_3 and V_4 , initially located at the center of a cubic cell with a side of 20 nm (in this case, the initial V_n concentration is about 2 appm), all segregated to the surface within one hour, while V_5 and V_7 took up to 10^6 s (about 10 days) to segregate to the surface. These results suggest that under a low radiation dose small vacancy clusters could not survive near the surface and will be absorbed by the surface at 1000 K.

To model the clustering and segregation of the V_n under different levels of radiation dose, we designed another two OKMC simulations where the initial V concentration was assigned to be 100 and 300 appm, respectively. After the system lasts for about one day, we examined the popular distribution of the vacancy clusters. We found that, as the initial concentration of the vacancy is 100 appm, only several V_5 and V_8 survived near the surface after one day. In the case of 300 appm, large vacancy clusters e.g. V_{12} and V_{15} appeared near the surface, implying that the clustering of vacancies and further growing of the cluster near the surface accompanied the segregation of small vacancy

clusters. Although the side of the cell is only 20 nm, vacancy clusters still accumulated near the surface. Therefore, surfaces in NP W may only efficiently alleviate defects accumulation in the system under a certain low radiation dose. This may be related to the small trapping range of the surface for the vacancy clusters (Figs. 8 and 9).

4. **Conclusion**

MS calculations and OKMC simulations have been combined to investigate the competition of the clustering and segregation of vacancies near the surface. Small vacancy clusters were found to have a high mobility comparable to that for the single vacancy. Mono-vacancies around the cluster prefer to bind with the cluster with reduced formation energy and diffusion energy barrier as diving forces. Cluster and become unstable near the (0 0 1) surface and get trapped by the surface via dissociation. At the operation temperature of 1000 K, V_1 , V_2 , V_3 and V_4 were observed to segregate to the surface within a time of one hour. Under a low radiation dose, surface (0 0 1) could act as a sink for small vacancy clusters, while under a high radiation dose, large vacancy clusters could survived near the surface and grow. We obtained several empirical expressions for the vacancy formation energy, binding energy and influence range as a function of the cluster size.

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Figure captions:

Fig. 1. The (0 0 1) surface structure after relaxation. The position of the first atomic layer is indicated by the red dashed line at the top. The atoms are colored with their potential energies as indicated by the color bar on the right side. The vacancy (represented by a green cubic) near the surface could directly segregate to the surface or bind with vacancy clusters and then diffuse towards the surface.

Fig. 2. (a) Stable configurations for small vacancy clusters. (b) Formation energies of the vacancy clusters in the bulk as a function of the number of vacancies n in the cluster.

Fig. 3. Binding energy (left axis) and influence radius (right axis) for the vacancy cluster V_n as a function of the number of vacancies, n .

Fig. 4. Energy variation on the migration path for small vacancy clusters in W bulk. The configurations of the cluster before and after migration are given to show the migration mechanism. The vacant sites are represented by green squares. The normal lattice sites are marked by blue circles. The total energy of each system with a stable defect configuration is selected as the reference energy.

Fig. 5. Migration barrier and transition time (left axis) for vacancy-type defects as a function of the number of vacancies n in the vacancy cluster. The transition time is calculated via $t = t_0 \exp(E_m/k_B T)$ where t_0 with a value of 10^{-12} s denotes the vibrational period of W atoms in the bulk. E_m means migration energy barrier. The Boltzmann constant k_B has a value of eV/K, and the absolute temperature T is set to 1000 K, which is the typical operation temperature of W as a diverter.

Fig. 6. Formation energy profile of the mono-vacancy near vacancy clusters as a function of the distance of the vacancy from the cluster center. The red dashed line indicates the bulk value of vacancy formation energy (3.75 eV). The black dashed lined indicates the minimal value of the formation energy.

Fig. 7. (a)–(f) Migration of the mono-vacancy around a stable vacancy cluster ($n=1, 2, 3, 5, 6, 7$). The lowest energy configuration for the is indicated by green squares. A vacancy (indicated by a black cubic) nearby migrates towards the cluster and then binds with the cluster and becomes one component of the cluster (indicated by a red cubic). (g) The average diffusion energy barrier for the V near a V_n as a function of n .

Fig. 8. (a) The artificially designed path for the V_2 migration towards the surface. The influence region of the surface is indicated by the two red dashed lines. (b) Formation energy profile for the

cluster V_2 near W (0 0 1) surface. (c) Diffusion energy landscapes for the V_2 migration towards the surface. The energy of the system with a bulk V_2 is chosen as reference.

Fig. 9. (a) The artificially designed path for the V_3 migration towards the surface. The influence region of the surface is indicated by the two red dashed lines. (b) Formation energy profile for the cluster V_3 near W (0 0 1) surface. (c) Diffusion energy landscapes for the V_3 migration towards the surface. The energy of the system with a bulk V_3 is chosen as reference.

Fig. 10. (a) Time needed for small vacancy cluster segregation to surface (0 0 1) at 1000 K drawn from OKMC simulations. (b) and (c) show the final population of vacancy clusters at 1000 K for an initial vacancy concentration of 100 and 300 appm, respectively. The evolution lasts for one day. In (b) and (c), vacancy clusters are shown by a green sphere with a radius proportional to the number of the vacancy in the cluster.